

THE ROLE OF NITROGEN IN GUN TUBE WEAR AND EROSION

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ABSTRACT

ARL has recently made discoveries in the area of interior ballistic propellant combustion product interactions with a gun tube bore. These discoveries were based on two hypotheses. The first was that the products could and are “dynamically nitriding” the bore of the gun, thus creating a nitride coating which inhibits the dissociation of CO and subsequently reducing the amount of carbon uptake. The second was that the combustion products richer in nitrogen have a lower temperature upon expansion in our experimental fixture as well as in a gun barrel. This is due to Joule and or Joule-Thomson cooling effects. Both of these hypotheses were proven and validated through numerical and experimental methods.

Higher nitrogen containing combustion products have definitively been shown to have relatively lower erosivity with respect to those having lower nitrogen content. These results have revolutionized the gun propellant development community in that for the first time there is guidance for erosivity control through propellant chemical constituent formulation.

1. INTRODUCTION

Gun tube wear and erosion has been a limiting factor in gun performance since their invention. Frederick Abel described gun tube erosion in the nineteenth century when he developed cordite. Since that time erosion has had a cyclic history between performance requirements, resulting erosion issues and subsequent palliatives. Historically, palliatives have been additives to the propelling charge to create a protective surface coating, a cool boundary layer, or a heat flux impediment. To date this is the preferred method of mitigating erosion given an existing weapon-charge system.

For over ten years ARL has been performing basic research in the area of gun tube wear and erosion, after a hiatus of about 15 years begun in the early 1980s. Propellant chemistry and the interaction of the combustion products with the gun tube wall has been the primary driver

of the research. Since WWII, it has been noted (Smith 1954) that propellants containing Nitramine are inherently more erosive than conventional propellants such as M30 (a triple based propellant having a similar adiabatic flame temperature). This claim was later verified (Ward, 1981). The reason for the high erosive behavior of this propellant was unknown. Surface chemical analysis of gun surfaces by Benet Laboratory (Kamdar, 1984), and ARL modeling (Conroy, 2001) assisted in developing an explanation for this behavior.

The primary finding of this previous work was that the carbon monoxide in the combustion product gas dissociated on the surface with a very small energy barrier. Subsequently, the free hydrogen scavenged the oxygen from the surface into water and the carbon diffused into the steel surface, resulting in a surface carburization (Conroy 2001). This transforms the steel into a cast iron, which reduces the surface melt temperature from 1723K down to 1423K. RDX based propellants have significantly higher amounts of carbon monoxide than the triple base propellant M30, which supports the hypothesis of CO dissociation and subsequent carburization.

The current paper describes work involving advanced propellant formulations having relatively high concentrations of nitrogen in the product species.

2. DISCOVERY OF DYNAMIC NITRIDING

Propellant erosivity characterizations were conducted in a blowout chamber fabricated from the breech and chamber of a 37-mm gun shortened and threaded to accept a retaining end cap for experimental samples. A photograph is shown in Figure 1 and sectional drawing is shown in Figure 2. This facility in various forms has been in use since WWII (Weigand, 1945).

Figure 3 shows a detail of an ARL erosion nozzle made typically of ASTM A723 alloy. The entrance to the nozzle is opposite to the throat. The nozzle profile was developed by continuously firing through a sample with a straight hole until the mass loss became consistent from one firing to the next.

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Fig. 1. Photograph of Army Research Laboratory 37-mm erosion fixture.

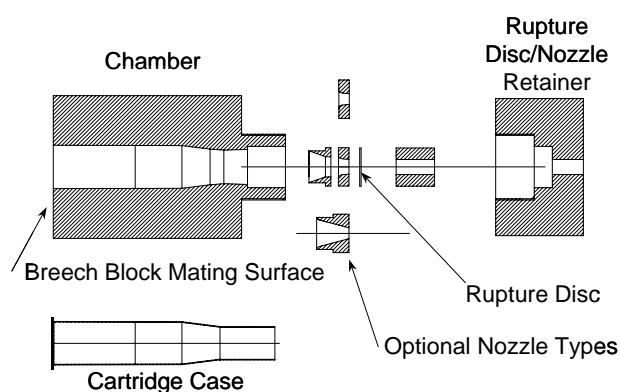


Fig 2. Drawing of Army Research Laboratory 37-mm erosion fixture.

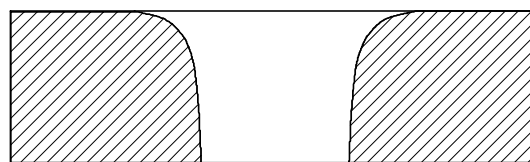


Fig. 3. ARL erosion fixture nozzle.

Selected
propellants
that

have recently been evaluated for erosivity are listed in Table 1. As the propellants were evaluated, all results supported the proposed carburization mechanism for erosion, until the testing of the Thiokol Gun Development Propellant TGD-002. While TGD-002 has an adiabatic flame temperature similar to that of M8, the CO/CO₂ ratio is about ten times higher than that of M8. Considering only the carburization mechanism, one would predict that TGD-002 erosion would be much higher than that of M8. What was found was that the TGD-002 erosion was actually lower than that of M8, as shown in Table 1. This effect was also noted in Indian Head Propellant IHGP-300, a 70% RDX system with a nitrocellulose and diazidonitrazapentane (DANPE) binder. As shown in Table 1, the mass loss from IHGP-300 was less than half of that of the M8, despite having a CO/CO₂ ratio eight times that of the M8.

It was hypothesized that high nitrogen propellants might “dynamically” nitride the inside bore surface of the

Table 1. Selected propellant properties and mass loss.

<u>Propellant</u>	<u>Chamber</u>			<u>Nozzle</u>			<u>Wear</u>
	Temp (K)	F(J/g)	Temp (K)	CO/CO ₂	N ₂ /CO	N ₂	(mg)
JA2	3450	1152	2569	2.53	0.35	0.126	90
PAP-8165	3419	1284	2444	8.29	0.78	0.271	62
TGD-9/2/9	3410	1291	2375	19.55	0.77	0.300	80
009+002	3410	1291	2375	19.55	0.77	0.300	104
TGD-019	3268	1296	2298	15.59	0.86	0.294	40
TGD-036	3191	1280	2238	18.26	0.84	0.292	57
TGD-035	3181	1273	2226	24.40	0.81	0.295	66
M43	3100	1186	2201	7.78	0.66	0.237	27
M30	3035	1080	2190	3.10	1.08	0.280	21
TGD-021	2795	1164	1995	22.27	0.91	0.305	5
TGD-009	2577	1072	1898	20.26	0.67	0.257	21

	<u>Chamber</u>			<u>Nozzle</u>			<u>Wear</u>
	Temp (K)	F(J/g)	Temp (K)	CO/CO ₂	N ₂ /CO	N ₂	(mg)
M8 (Ward, 1982)	3768	1168	2922	1.44	0.49	0.146	241
JA-2/ RPD351	3743	1172	2892	1.50	0.48	0.143	251
TGD-002	3718	1354	2643	14.88	0.84	0.324	193
IHGP-300	3725	1333	2730	4.13	0.89	0.284	114

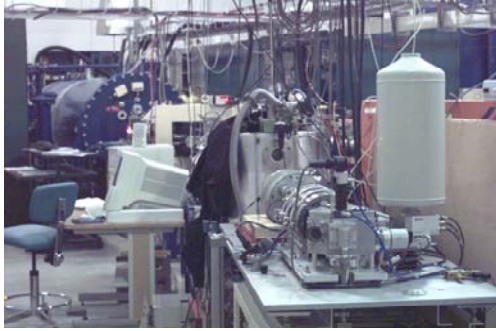


Fig. 4. ARL ion accelerator facility.

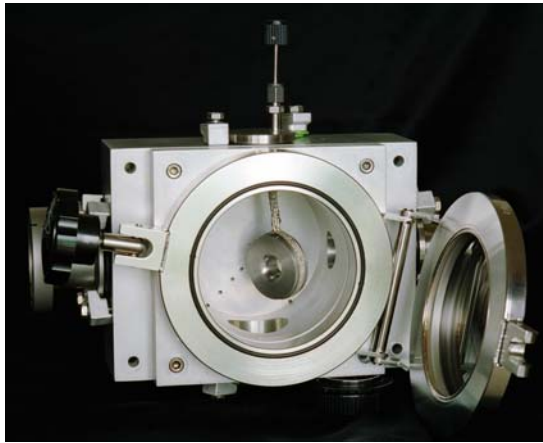


Fig. 5. Nuclear Reaction Analysis chamber.

erosion nozzle during firing. This nitriding could occur over milliseconds, whereas typical gaseous nitriding can take hours or days. We investigated this possibility by measuring the nitrogen content on the surface of test nozzles after firing, using resonant nuclear reaction analysis at the ARL ion accelerator facility shown in Figure 4. An energetic beam of protons was directed onto the surface, inducing the $^{15}\text{N}(p,\gamma)$ reaction, and the characteristic gamma rays were detected using a scintillation detector near the analysis chamber (Figure 5). Since this reaction occurs only at a particular ion energy, the beam energy was increased to query the nitrogen concentration at increasing depths into the sample; the gamma yield could then be calibrated to give a depth profile of nitrogen in the gun steel. Figure 6 shows atomic nitrogen content vs. energy (depth) at various locations on the inner surface of an ARL erosion nozzle, which had high nitrogen propellant products exhausted through it. The resultant concentrations are as high as 9 atomic percent. This places the nitriding at Fe_4N levels.

Possible explanations for how surface nitriding can assist in erosion reduction come from surface chemistry, as well as from the binary phase diagram of iron nitride.

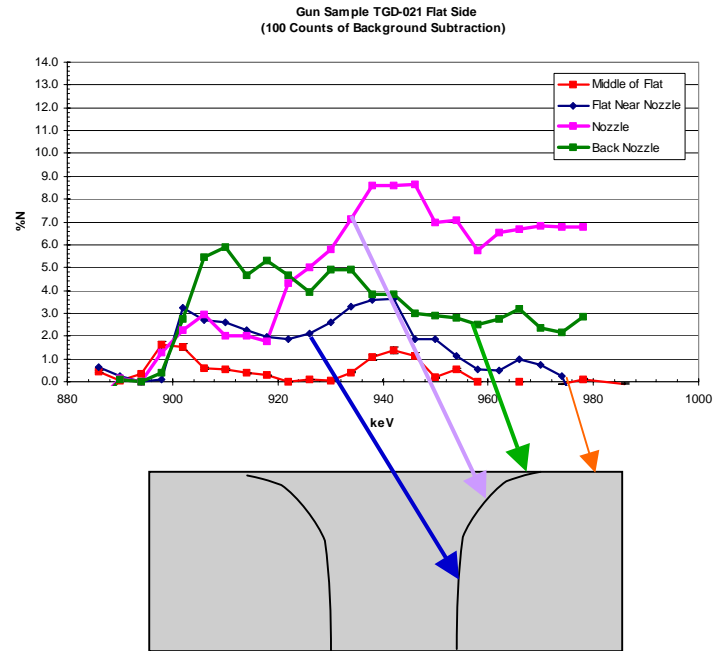


Figure 6. Depth profiles of nitrogen taken using nuclear reaction analysis [NRA] at four different positions relative to the inner exposed surface of the test nozzle.

Literature suggests that nitrogen on a steel surface may inhibit dissociation of CO (Poniec, 1981). Thus dynamic nitriding can act to interrupt the primary driving reaction of the chemical erosion mechanism, which is the adsorption / dissociation of carbon monoxide on the surface. Also, the presence of nitrogen takes up sites in solution with iron and could inhibit the subsurface diffusion of the free carbon into the steel.

Carburization of the gun reduces the melt temperature of the surface from 1723K to 1423K. The binary iron-carbon phase diagram in Figure 7 shows how this reduction in melt temperature occurs. The virgin 4340 or ASTM 723 steel begins with about 0.4% carbon. As carbon is added to this mixture the melt temperature continuously reduces until it stabilizes at 1423K, which defines the boundary between cast iron and steel. Once the carbon concentration exceeds 2.1% the material is then cast iron. Erosion calculations have shown that the surface can saturate with carbon providing the best boundary source available for diffusion (Conroy, 2001). This enables the formation of substrate iron carbide at the maximum rate possible. As the ballistic cycle progresses the surface temperature rises, all the while carbon is diffusing and creating Fe_3C . Once the surface temperature reaches 1423K the energy balance on the surface including phase transformation results in macroscopic melting. This is one of the primary mechanisms for the removal of surface and interfacial material (Conroy, 2001).

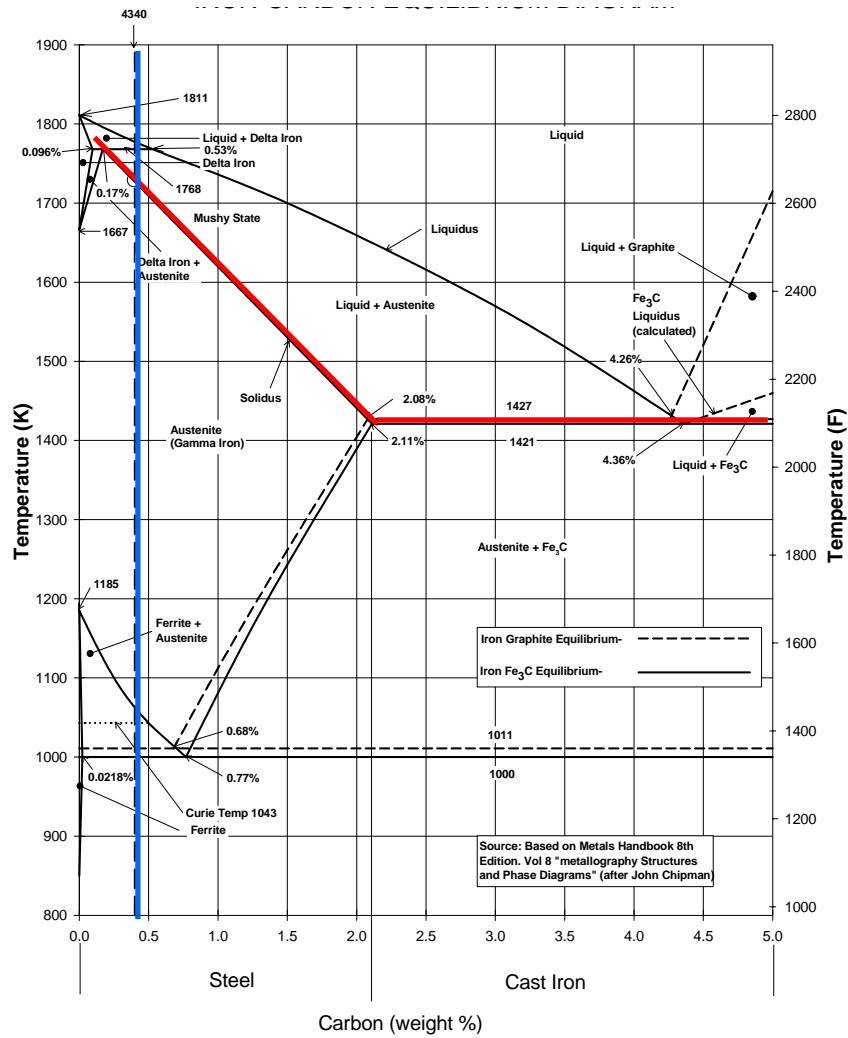


Figure 7. Iron / carbon phase diagram [Metals Handbook 1973].

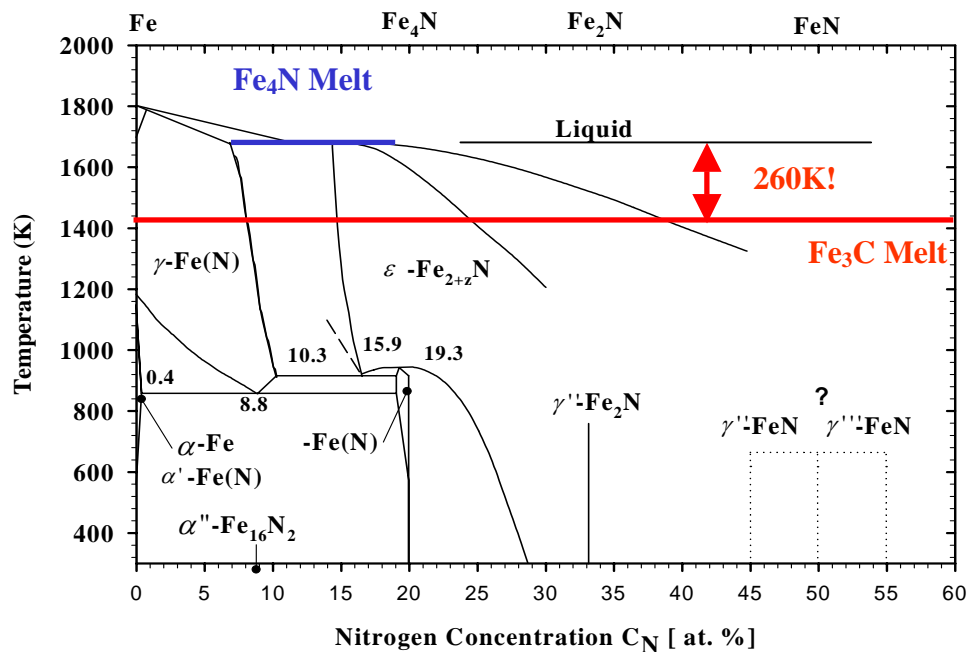


Figure 8. Iron / nitrogen phase diagram [From Guillermet & Du, 1994].

The iron / nitrogen phase diagram presented in Figure 8 (Guillemet & Du, 1994) demonstrates how nitrogen in solution with iron can be more resistant to erosion than carbon in solution with iron under ballistic conditions. The phase transition from solid to liquid for iron nitride is shown as a constant 1683K, between 7 and 20 atomic percent nitrogen. This presents a remarkable 260K increase in the surface melt temperature over that of the iron carbide at 1423K. For chrome plated tubes this increase is obtained at the weakest point of the system, which is at the interface between the chrome and steel at the bottom of cracks in the chrome coating (Conroy, 2001). This represents an enormous opportunity for improvement for gun systems in terms of tube life and possibly system performance.

3. TEMPERATURE REDUCTION DUE TO EXPANSION

In addition to the dynamic nitriding, nitrogen can also reduce the product gas temperature in regions of expansion due to higher intermolecular attraction forces and larger product molecular size through the Joule and Joule-Thomson effects.

Two processes have been considered for their effect on temperature reduction: isenthalpic expansion (throttling), and free expansion of gases (Sears, 1975; van Wylen, 1985). These processes relate in some respects to the expanding gases found in a gun during the interior ballistic cycle. The following analysis is an attempt to physically describe why the gases cool upon expansion as well as the effect that mixture composition might have upon the expanding combustion products.

3.1 Isenthalpic Expansion

The familiar expression for the Joule-Thomson coefficient for an isenthalpic process may be expressed in the following fashion assuming van der Waals equation of state.

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h = \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_p - V \right) = - \frac{1}{C_p} \left(\frac{RTv^3b - 2av(v-b)^2}{RTv^3 - 2a(v-b)^2} \right). \quad (1)$$

When μ is equal to zero in this relationship, the function defines the temperature inversion curve, at which a specific species will cool if expanded when initially below the inversion temperature and heat if expanded when initially above the inversion temperature. The relationship of the inversion temperature is.

$$T_i = \frac{2a(v-b)^2}{Rv^2b}. \quad (2)$$

From Table 2, the inversion temperature shows that reducing or replacing the hydrogen with nitrogen would result in a larger temperature reduction during an isenthalpic process.

Table 2. Van der Waals constants comparisons of products.

Product Species	van der Waals constant a (kJm ³ /kmole)	van der Waals constant b (m ³ /kmole)	Inversion temp. (K) (v = 0.4m ³ /kg)
H ₂	25	0.0266	1000.
N ₂	137	0.0387	7803
CO	148	0.0395	8610
CO ₂	365	0.0428	23032
H ₂ O	553	0.0305	24656

Unfortunately, there would also be a penalty in performance for such a propellant, because the impetus will suffer as the average molecular weight of the products is increased, as shown in equation 3.

$$IMPETUS = \frac{RT}{MW} \quad (3)$$

3.2 Free Expansion

What happens in a gun is closer to expansion with work on the projectile, and gases along with losses such as heat and friction to the barrel. To obtain an idea of what happens in the ARL experimental fixture we might assume an adiabatic system with no work performed, neglecting the heat transport and the lightweight rupture diaphragm. Free expansion might be more representative of what occurs before the throat of the nozzle. In this case the internal energy is constant and the change in volume is accompanied by a change in temperature. Differentiating the internal energy with the aforementioned constraints as well, as constant mass, results in

$$dU = \left(\frac{\partial U}{\partial T} \right)_{V,N} dT + \left(\frac{\partial U}{\partial V} \right)_{T,N} dV. \quad (4)$$

If we assume the van der Waals equation of state

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT, \quad (5)$$

the following relationship can be derived describing the change in internal energy with respect to volume,

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{an^2}{V^2}. \quad (6)$$

This implies that the larger the intermolecular attractive force the larger the temperature decrease will be. Therefore, from Table 2, the more hydrogen that can be replaced by nitrogen in the combustion products the lower the temperature will be in the entrance region of the nozzle. And once again this implies a negative impact upon the impetus of the propellant as equation 3 shows.

A general conclusion is that a reduction in expansion temperature due to the replacement of hydrogen with

nitrogen in the products will be accompanied by a reduction in impetus for a gun propellant. While the erosion might be reduced through the Joule and or Joule-Thomson effects, the impetus of the propellant will decrease through the overall increase in average molecular weight. Thus there is an apparent balance between erosion and performance. However, it may be possible to increase the loading density through advanced charge designs to overcompensate for the reduced impetus, which would result in an overall performance increase while reducing/minimizing the erosion.

4. PRENITRIDING

The discovery of dynamic nitriding leads to an exciting corollary: prenitriding a gun tube could provide significant benefits. Nitriding has been performed for over half a century on gun tubes (Di Pietro, 1947). The M242 Bushmaster cannon has specifications stating that the bore can be either chrome plated or nitrided. Current nitriding results in a very reproducible wear and barrel life in comparison to chrome plating, which is sometimes less reproducible (Robert Waterfield (ATK), private communication). Unfortunately, nitrided M242 barrels do not have the erosion life of the chrome barrels. We may now be able to explain this result.

Conventional nitriding produces an error function distribution of nitrogen in the surface. This distribution ranges from a hard white layer (FeN) on the surface, through all the substoichiometric nitrides of iron, to deep into the iron where there is no nitrogen present. This implies a melting temperature range from as low as 1200K at the surface up to the optimal temperature of 1683K where the nitrogen content ranges from 7 to 20 atomic percent (Figure 8). Unfortunately by the time the erosion progresses until the surface has an optimal melt

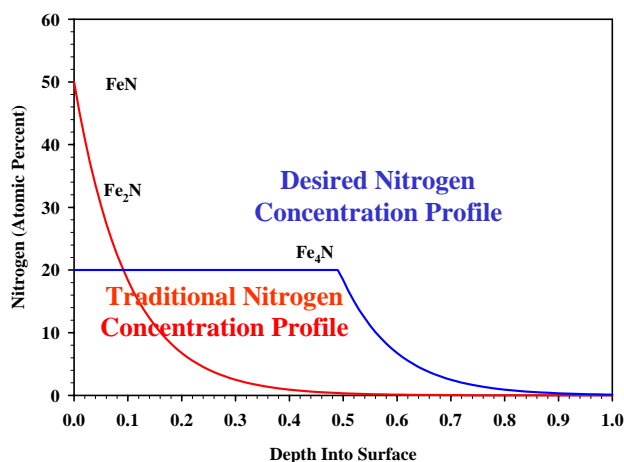


Figure 9. Traditional and preferred nitrogen profiles.

temperature there is not much nitrogen left as shown in Figure 9 in the traditional nitride profile.

Conversely, if the nitrogen profile appears as in the desired nitrogen profile of Figure 9 then the benefit is realized throughout the life of the gun tube. This profile may be reached through laser nitriding (Schaaf, 2002).

The benefit could also be realized if the surface of chromed or otherwise coated tubes were pre-nitrided to protect the interface between the coating and substrate steel from degradation when cracks occur.

5. CONCLUSIONS

The dynamic nitriding and the temperature reduction due to propellant gas expansion have been shown to lead to remarkably reduced erosion resulting from propellant formulations having relatively high nitrogen content.

The new energetic propellant formulations that include “high nitrogen” ingredients can lead to reduced gun barrel erosion for both legacy systems and future armaments. This discovery is applicable to every gun system in the DoD inventory, including mortars. Furthermore, for the first time propellant formulators have the ability and guidance to produce inherently less erosive propellants through energetic ingredient selection.

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